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Thermal stability of biodiesel and its blends: A review

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A B S T R A C T

The vegetable oil, fats and their biodiesel suffer with the drawback of deterioration of its quality during long term storage unlike petroleum diesel due to large number of environmental and other factors making the fuel stability and quality questionable. There are various types of stabilities like oxidation, storage and thermal, playing key roles in making the fuel unstable. The present paper is an attempt to review the work done so far on the thermal stability of biodiesel and their blends with diesel under different conditions. The mechanism of thermal deterioration of vegetable oils, various methods of stability measurement including a new proposed method based on Karl Fischer coulometer, an alternative to conventional Rancimat test has been discussed. No correlations have been found in the literature among the results of various methods used. The effect of antioxidants on the stability parameters has also been discussed. TGA/DTA has been found as an effective method to check the deterioration of oil with respect to temperature using activation energy and order of reaction as the parameter to monitor the deterioration of oil.

Contents

1. Introduction

Biodiesel is a mixture of fatty acid mono-alkyl esters with relatively high concentrations of long-chain mono- and polyunsaturated compounds to promote better cold flow properties [1–3]. Methyl esters from SO (SME), for example, are typically composed of mainly C-16 and C-18, where 80–85% (w/w) of the total mixture is unsaturated FAME [4]. The presence of such mono- and polyunsaturated compounds make ME highly susceptible to oxidative degradation [5].

Transesterification reaction of oil or fats with short chain alcohol usually methanol and ethanol, leads to the production of mixture of corresponding mono-alkyl esters defined as biodiesel. Since the biodiesel has the fatty acids compositions similar to the parent oils or fats with considerable amount of unsaturated fatty acids, its oxidative stability is affected, especially, during its long-time period storage [6,7]. Exposure to UV irradiation, high temperature and presence of metal traces (contaminants) can reduce the overall stability of the biofuel, thereby, affecting its quality and hence marketability. The stability parameters of the biodiesel like kinematic viscosity, cetane number and acid value are affected during oxidative degradation [6,8,9].

Apart from a number of parameters affecting the stability of vegetable oils as well as biodiesel, the temperature has significant effect on oxidative degradation, perhaps, due to the enhancement

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Nomenclature

F10	Irgalube
L135	Irganox
PO	palm oil
HO	hydraulic oil
TAN	total acid number
IV	iodine value
TGA	thermo gravimetric analysis
n	order of reaction
k	reaction rate constant
x	extent of conversion or fractional weight loss
w_0	original weights
w_t	current weights
w_∞	final weights
T	temperature
t	time
E_a	activation energy
R	gas constant
ASTM	American society of testing materials
DTA	differential temperature analysis
PDSC	pressurized-differential scanning calorimetry
TG	thermo gravimetry
OSI	oil stability index
IP	induction period
C/H	carbon/hydrogen mass ratio
HPLC	high-performance liquid chromatography
AV	acid value
PV	peroxide value
KF	Karl Fischer
FAME	fatty acid methyl ester
C-16:0	palmitic acid
C-18:1	oleic acid
UV	ultra violet
SME	soybean oil methyl ester
PPM	parts per million
OSIcalc	oxidation stability index calculated
UCOME	used cooking oil methyl ester
MO1	methyl oleate
SO	soybean oil
MO	mixture of soybean oil and palm oil
h	hours
ml	milliliter
l	liter
ν	kinematic viscosity

in the rate of degradation thereby playing an important role in destabilizing the fuel quality which is the subject of the present paper. Thermal stability involves the measurement of the tendency of a fuel to produce asphaltenes, when exposed to high temperature conditions. These asphaltenes are tar like resinous substances generated in the fuel and plug the fuel filters of the engines when used as fuel [10].

2. Mechanism of thermal stability

At sufficiently high temperatures, the methylene-interrupted polyunsaturated olefin structure will begin to isomerize to more stable conjugated structure. Once this isomerization has begun, a conjugated diene group from one fatty acid chain can react with a single olefinic group from another fatty acid chain to form a cyclohexene ring [11,12]. This reaction between a conjugated di-olefin and a mono-olefin group, called Diels Alder reaction and shown in Fig. 1, is known as Diels Alder reaction which becomes important at temperatures of 250–300 °C or more and the reaction products formed are called dimmers [13–15].

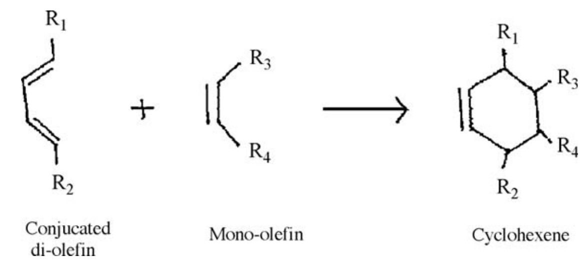


Fig. 1. Diels Alder reaction.

Thermal polymerization can also form trimers by the reaction of an isolated double bond in a dimer side chain with a conjugated diene from another fatty oil or ester molecule (a Diels Alder reaction) [15]. However, an earlier study provided the evidence supporting the non-Diels Alder coupling of two-side chain olefin groups from a dimer and a fatty oil molecule [13]. Thermal polymerization is characterized by rapid reduction in total unsaturation as all the three olefin groups become one. When linseed oil was thermally polymerized at 300 °C, initial polymerization resulted in dramatic reduction of total unsaturation as measured by IV. However, no increase in molecular weight was observed. This was found to be due to an intra-molecular Diels Alder reaction between two fatty acid chains in the same triacylglyceride molecule. This may have ramifications for biodiesel made from used cooking oils that are subjected to temperatures in excess of 300 °C when used in high-pressure cookers. If such intramolecular dimers were to form during such thermal stressing, they would retain their linking when transesterified to methyl esters for use as biodiesel. The resulting species would be a di-ester with a molecular weight about twice that of a normal biodiesel ester molecule. If such biodiesels (i.e. yellow greases) were not distilled, these dimers would appear in the final fuel. No work has however been reported that indicates the presence of such dimers in used cooking oils and if so, their effect on fuel properties of the corresponding non-distilled biodiesel fuels. The potential existence of such dimeric species in non-distilled yellow grease biodiesel has not been addressed in the published literature pertaining to the U.S. biodiesel manufacturing/marketing industry [15].

The thermal polymerization may be of limited importance in biodiesel, which is heated repeatedly by the engine and recycled to the fuel tank before actual combustion. The thermal polymerization therefore does not impact the storage stability of biodiesel.

3. Effect of high temperature on biodiesel stability

Vegetable oils consist of natural antioxidants that tend to increase the stability of fuel but as the vegetable oils are subjected to higher temperature conditions, the natural antioxidants present in the oil start deteriorating at a faster rate, thereby, decreasing its stability. As the biodiesel comes in contact with engine, it gets heated leading to the decrease in fuel stability.

Bondioli et al. [16] evaluated the storage stability of biodiesel at different temperatures. Samples were kept at two different temperatures (20 °C and 40 °C) during experimentation and it was found that increase in PV was higher at lower temperature while using the same container.

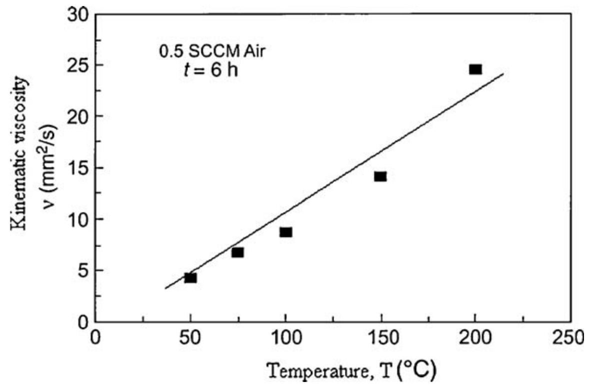


Fig. 2. Kinematic viscosity (ν) of oxidized SME at 40 °C vs reaction temperature (T) [17].

Dunn [17] has evaluated the effect of oxidation under accelerated conditions on fuel properties of methyl soyate. SME samples were collected from four different fuel producers. Oxidation reactions were conducted in the laboratory under varying time and temperature conditions. In order to determine the effects of oxidative degradation on biodiesel fuel, the reaction conditions were designed to produce measurable changes in most fuel properties in a relatively short time. Samples were placed in a three-necked round-bottomed flask and heated by a variant controlled mantle. Clean and dry air was bubbled slowly throughout the reaction using water-cooled condenser to minimize the evaporative losses. Air flow was manually regulated at a constant rate of 0.5 standard cm^3/min (SCCM) with stirring of the reaction mixture to minimize wall effects and to keep the mixture homogeneous throughout the duration of the reaction. The results as shown in Figs. 2–4 indicate that with increase in reaction temperature, viscosity, acid value and peroxide value respectively increased significantly including specific gravity whereas, the cold flow properties were minimally affected for temperature up to 150 °C.

Fig. 2 shows the variation of kinematic viscosity of SME calculated at 40 °C with respect to reaction temperature. It is clear from the figure that the viscosity increases linearly as the temperature of the reaction is increased. The possible reason for this behavior may be due to Diels Alder reaction which leads to the formation of polymers at higher temperatures.

The variation in acid value with respect to reaction temperature as given in Fig. 3 which shows that with increase in reaction temperature, the acid value decreases linearly. Thermal degradation is the responsible for increase in AV with increasing temperature.

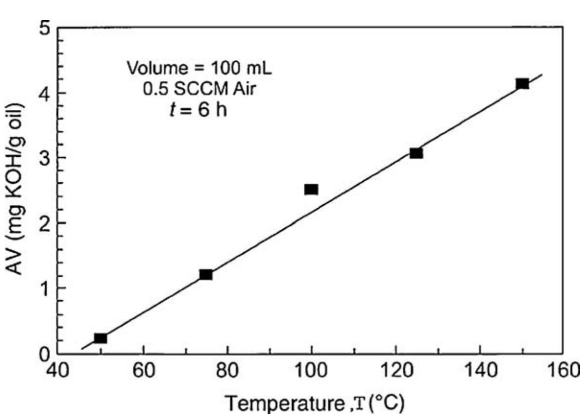


Fig. 3. AV of oxidized SME vs reaction temperature (T) [17].

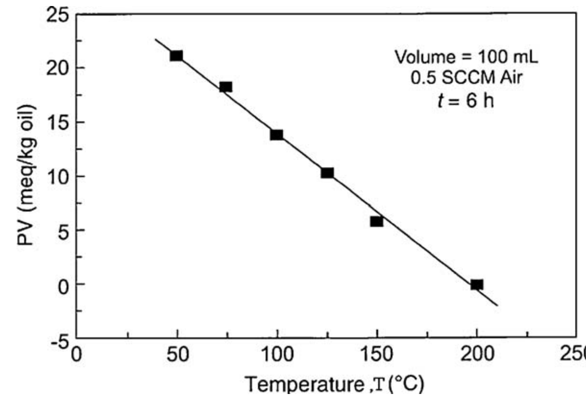


Fig. 4. PV of oxidized SME vs reaction temperature (T) [17].

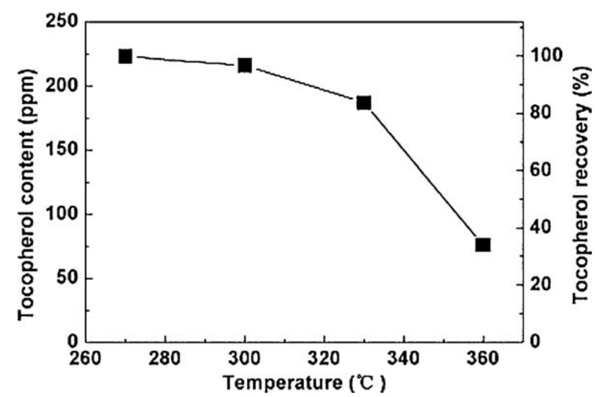


Fig. 5. Effect of temperature on the tocopherol content in rapeseed biodiesel as treated in supercritical methanol [18].

The variation of PV with reaction temperature is shown in Fig. 4. It is clear from the graph that as the reaction temperature increases, the PV decreases linearly, perhaps, due to the absence of oxygen or acceleration of decomposition of hydroperoxides with increase in temperature.

Xin et al. [18] studied the oxidation stability of biodiesel prepared from supercritical methanol method. The effect of temperature on the tocopherol content in biodiesel was studied by choosing rapeseed biodiesel as a representative biodiesel. Rapeseed biodiesel was exposed to supercritical methanol at 270 °C/17 MPa, 300 °C/20 MPa, 330 °C/37 MPa, and 360 °C/47 MPa for 30 min, the remaining tocopherol content in rapeseed biodiesel was measured and the results are shown in Fig. 5 which indicates that with increase in temperature above 300 °C, the remaining tocopherol decreased with an increase in temperature. While a further temperature increase led to the significant reduction in the tocopherols content.

These observations clearly indicated that the tocopherol in biodiesel is not stable at a temperature >300 °C. The biodiesel obtained through supercritical method will therefore have overall lower stability compared to biodiesel prepared using other methods of transesterification [16,18–20].

Dunn [19] studied the effect of temperature on the oil stability index (h) of biodiesel and found that an increasing temperature accelerated the oxidation reaction causing a decrease of OSI as shown in Fig. 6.

The variation in calculated oxidation stability index as a function of oxidation stability (OSIcalc) of SME, UCOME and MO1 with respect to reaction temperature is shown in Fig. 6 which indicates the decrease in OSIcalc as the temperature is increased. At higher temperature, the rate of polymer formation is increased

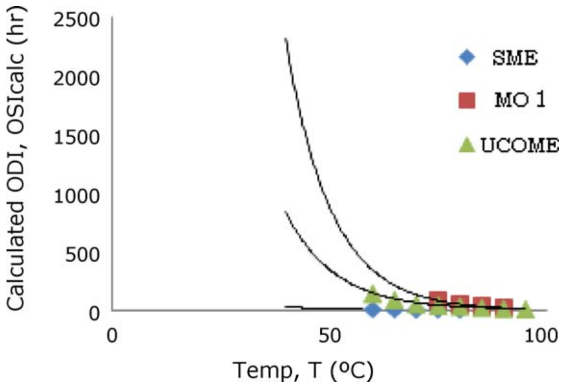


Fig. 6. OSIcalc of SME, UCOME and MO1 as a function of temperature (*T*) [19].

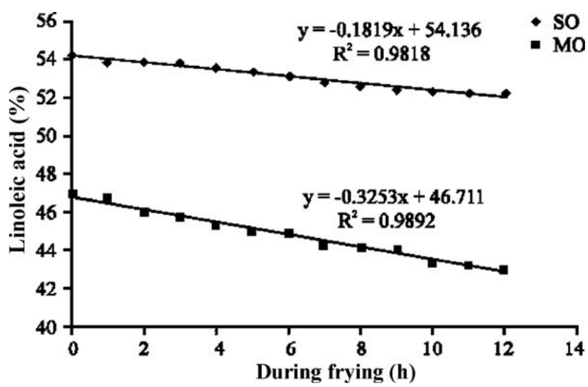


Fig. 7. Relationship between linoleic acid degradation and the frying time of SO and mixture of MO [20].

resulting in the increase in viscosity and acid value and decrease in PV as reported by Dunn [17] and ultimately in the decrease in the OSI.

Nzikou et al. [20] studied the thermal stability of vegetable oils during frying and found a decrease in Linoleic acid contents with increase in frying hours of oil.

Relationship between % linoleic acid with frying hours for SO and MO frying temperature of 180 °C as shown in Fig. 7 indicates that the linoleic content decreases with increase in frying hours due to lipid oxidation [20]. It is clear from the figure that the relation between % linoleic acid and frying time with standard deviation (R^2) as 0.9818 and 0.9892 can be used to assess the stability aspect to the extent of 98.18% and 98.92% for SO and MO respectively.

The relationship between viscosity at 20 °C and frying hours for both SO and MO at frying temperature of 180 °C is given in Fig. 8 which shows that the viscosity of oils increases with increase in frying days due to the formation of high molecular weight polymers. Higher the viscosity of frying oil, higher will be the degree of deterioration [20]. This is in agreement with the findings of Dunn [17]. The above figure shows that the relationship with higher values of standard deviation (R^2) as 0.9893 and 0.991 can be used to the extent of 98.93% and 99.1% for SO and MO respectively.

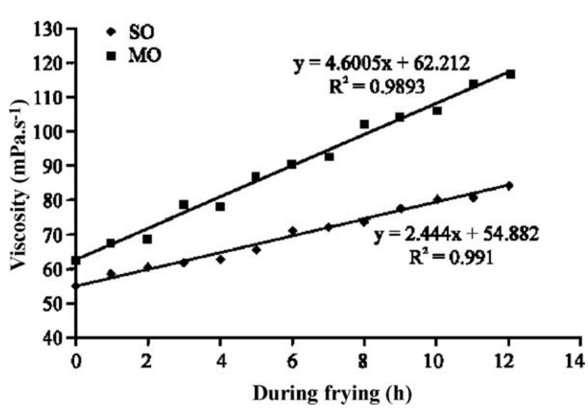


Fig. 8. Relationship between viscosity (measured at 20 °C) and the frying during for SO and mixture of MO [20]

4. Measurement of thermal stability

Various procedures designed to accelerate the oxidative and/or thermal instability of fatty oils have been developed or adapted from similar procedures used in other industries most notably the fuels and lubricants industries. However, the most important procedures related to thermal stability are given below:

4.1. Rancimat method

The length of time before the rapid acceleration of oxidation is the measure of the resistance to oxidation and is commonly referred to as the 'induction period, or Oxidative Stability Index (OSI)

The OSI test is the commonly used test in Europe where biodiesel fuels should meet the specification of an induction period (IP) of at least 6 h when tested at 110 °C [21]. The Metrohm Rancimat apparatus is frequently used to measure OSI and the term "Rancimat" and "OSI" are often used interchangeably in the literature while referring to the test method. OSI, commonly used in experiments, requires to pass air through a heated sample of the fatty oil or ester [16,22,23]. The air coming out of the sample is finally passed through water contained in a tube fitted with a conductivity meter (Fig. 9). A sharp rise in conductivity is interpreted as indicative of the formation of short chain, water soluble carboxylic acids, i.e., secondary oxidation products (Fig. 12). Studies have indicated that the primary acidic species formed in the Rancimat OSI test is formic acid. The mechanism of decomposition of hydroperoxides to form formic acid has been explained by Hasenhuettl et al. [25]. An alternative approach has been reported where chemiluminescence is used to monitor the oxidation during the OSI test [24].

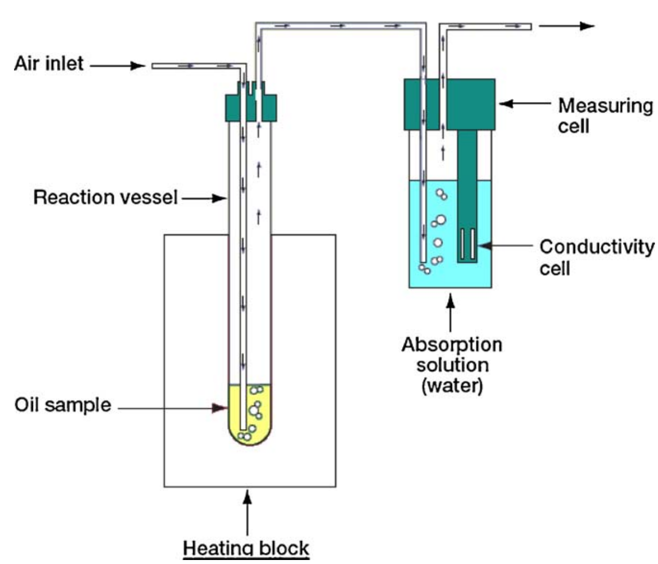


Fig. 9. Schematic of Rancimat test [25–27].

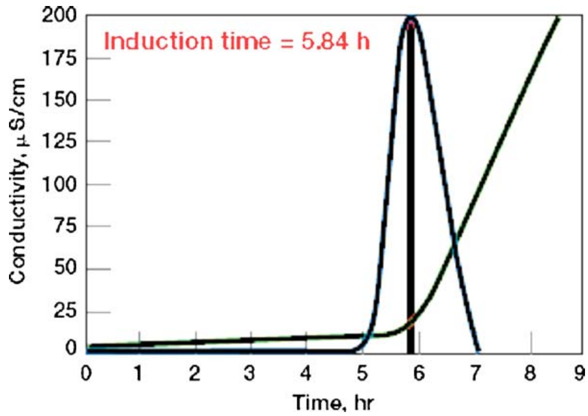


Fig. 10. Conductivity vs time in Rancimat test.

Fig. 10 shows that as the temperature of Rancimat test is increased, the value of induction period decreases. The period of sudden increase in conductivity is called as induction period (e.g. 6 h in this case). Different oils have different induction periods. Several studies have shown that when the Rancimat test is conducted at different temperatures, the logarithm of the induction period (IP) will be a linear function of test temperature, i.e. plots of log (OSI IP) vs T give straight lines [25–28]. This suggested that biodiesel stored at lower temperature is favorable for long-time storage of biodiesel without degradation. The Rancimat test has used to measure the thermal stability by not using an airflow but by measuring the polymer content in 8 g biodiesel sample after 6 h at 200 °C [21]. The test seems to be suitable for use in terms of repeatability and easiness to handle.

Paolo et al. [16] found that the decrease in Rancimat induction period is faster at 20 °C than 40 °C with respect to time, though the difference between two temperatures is very less. This may be due to high PV and high AV at lower temperature.

Xin et al. [28] studied the effect of temperature on induction period of safflower oil and found that as the reaction temperature increases, induction period is decreased. The relationship between logarithms of induction periods (ln IP) determined by Rancimat method with temperature is reported for various biodiesels and mixtures of biodiesel are shown in Fig. 11 [28].

Intercepts of lines represent that the biodiesels having the same induction period at 110 °C, but with different long-time storage stabilities. As a result, the Rancimat method gives only approximate information about the stability of biodiesel and long

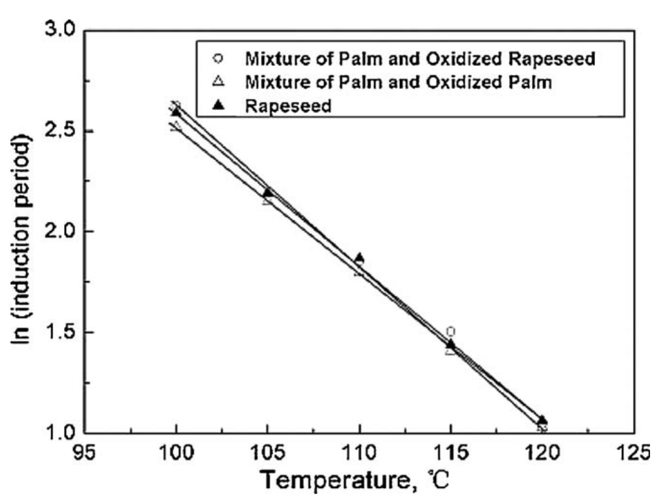


Fig. 11. ln IP vs temperature for various biodiesel and mixtures of biodiesel [28].

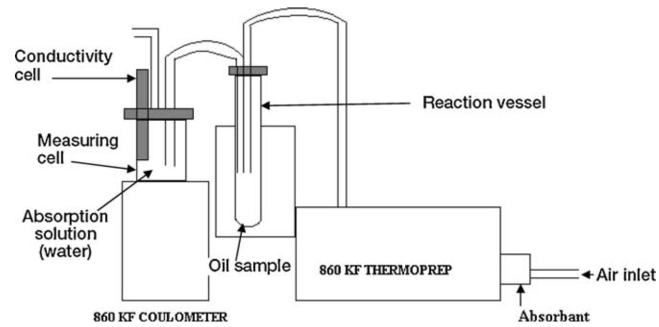


Fig. 12. Alternative Rancimat test using Karl Fischer (831 KF).

induction period does not necessarily represent the long storage stability because of the different temperature coefficients for biodiesel obtained from different sources.

Alternatively, the Rancimat test can also be performed manually using the Karl Fischer Coulometer make Metrohm (model no. 831 KF) as shown schematically in Fig. 12.

There is an internal pump to suck the air. The air flow rate and the temperature of the oven can be precisely adjusted. A well calibrated digital conductivity meter can be installed externally in the measuring cell. The apparatus can be used to check the oxidation as well as thermal stability. Air supply is closed at the time of measurement of thermal stability. However, the remaining part of the experimentation is same as that of Rancimat test. Therefore, it may be used as an alternative method as Rancimat test, though the validation of the former is under progress in our research laboratory.

4.2. ASTM method

4.2.1. D 6468-08 [29]

It gives an indication of thermal oxidative stability of distillate fuels when heated to high temperatures occurring in recirculating engines or burner fuel delivery systems. Results have not been substantially correlated to the engine or burner operation. The test method can be useful for the investigation of operational problems related to fuel thermal stability.

In the test, two samples of 50-ml each of filtered middle distillate fuel are aged for 90 or 180 min at 150 °C exposed to air. After aging and cooling, the fuel samples are filtered and the average filterable insolubles are estimated by measuring the light reflectance of the filter pads. The 100% and 0% extremes of the reflectance rating range are defined by an unused filter pad and a commercial black standard respectively.

The test method makes use of a filter paper with a nominal porosity of 11 μm which does not capture all the sediment formed during aging but allows differentiation over a broad range. Reflectance ratings are also affected by the color of filterable insolubles that may not correlate with the mass of the material filtered from the aged fuel sample. Therefore, no quantitative relationship exists between the pad rating and the gravimetric mass of filterable insolubles.

ASTM D6468 has existed in nearly the same form (albeit different names) for over 60 years. Its very short time of 90-min test time makes it a very attractive test for quality assurance and quality control. The 150 °C test temperature makes this test quite severe. There is no active addition of air or oxygen to the fuel during testing so this test is not as useful for measuring oxidation stability. Also, this test method has historically relied on estimating the amount of insolubles formed based on the darkness of the material trapped on a filter pad. Biodiesel insolubles tend to be far less dark in color than petroleum diesel and as such, are more

difficult to quantify using optical methods. Gravimetric measurement of insolubles provides more reliable quantification. Biodiesel tends to be very thermally stable but less stable oxidatively when compared to petroleum diesel. This test method does not provide a useful discrimination between biodiesel fuels of varying quality. This test may, however, be useful for B20 but more work is still required to be done as the repeatability of results is not acceptable [21].

4.2.2. D 5304-06 [30]

A 100 ml aliquot of filtered fuel is taken in a borosilicate glass container placed in a pressure vessel already preheated to 90 °C. The pressure vessel is pressurized with O_2 to 800 kPa (absolute) (100 psig) for the duration of the test. The pressure vessel is placed in a forced air oven at 90 °C for 16 h (taking all normal precautions while using oxygen under pressure and at high temperatures in the presence of combustible liquids. Appropriate shielding should be used for any containers under pressure. The container is pressurized and depressurized slowly using appropriate personnel shielding). After aging and cooling, the total amount of fuel insoluble products is determined gravimetrically and corrected according to blank determinations.

Schematic of filtration system is shown in Fig. 13 used to filter the sample and to measure the filterable insolubles. It consists of a vacuum pump to create vacuum within the receiving flask at a pressure of 800 kPa (absolute). It consists of a receiving flask of 1.5 l to which the filtration apparatus fits into, equipped with a side arm to connect to the safety flask to which vacuum pump is connected.

Several studies have found the excellent thermal stability result when measured by ASTM D6468 [31–34]. In one study, the method was modified to measure the filterable insolubles formed during the 90 °C and 180 min thermal stressings. All the neat biodiesel and blends of biodiesel with No. 2 diesel fuel were found to be very stable. The BIOSTAB project also showed excellent thermal stability using D6468 [21]. However, when the severity of thermal stability test procedure was increased using Rancimat apparatus at 200 °C without airflow, significant evidence of instability was observed in terms of significant increase especially, in total acid number (TAN) and viscosity in all the eight methyl ester samples. Polymer levels were also greatly increased with final values ranging from 5.5% to 18.2% (w/w). The biodiesel fuels were found to have good thermal stability as they are derived from vegetable oils known to be well-suited for high temperature cooking applications such as deep-fat frying and pressure cooking [21].

4.3. TGA/DTA method

Thermal stability of oils depends on their chemical structures. Oils with a high proportion of unsaturated fatty acids are less stable than the saturated ones [35]. In the recent years, thermal analysis was successfully used to study the physical properties, chemical reaction and the thermal stability of oils. Thermoanalytical methods specially thermogravimetry analysis (TGA) has the advantages of being precise, sensitive and fast needing small amount of sample [35].

Thermo analytical methods include a group of techniques in which the thermal behavior or thermal properties of a material are determined as a function of temperature. The thermal tests measure the change of weight and enthalpy as the sample is heated. TGA has been used extensively in polymer science for measurement of degradation of polymer [36–38]. The equipment continuously monitors the loss of sample weight while the sample is heated in isothermal or dynamic conditions. Thermal analysis techniques have been used for the characterization of edible oils and fats by studying several properties such as thermo-oxidative behavior and stability [39–41], specific heat [42], thermal decomposition activation energy [43], temperature and enthalpy of crystallization [44–47], effect of antioxidants on thermal stability of oils [43,48], degree of unsaturation from melting and crystallization oil profile curves [49] and high-pressure oxidation induction period measurements [50].

Thermogravimetric analysis is normally carried out either in the presence of air or in an inert atmosphere, e.g., N_2, He, Ar and the weight loss is recorded as a function of increasing temperature. The measurements are, sometimes, performed in O_2 atmosphere (1–5% O_2 in N_2 or He) and sometimes in a lean oxygen atmosphere (1–5% O_2 in N_2 or He) to slow down oxidation process. Some instruments also record the temperature difference between the sample and one or more reference pans (differential thermal analysis or DTA) or the heat flow into the sample pan compared to that of the reference pan (Differential Scanning Calorimetry, or DSC). The later can be used to monitor the energy released or absorbed via chemical reactions during the heating process.

In most cases, TGA analysis is performed in an oxidative atmosphere (air or oxygen and inert gas mixtures) with a linear temperature ramp. The maximum temperature is selected so that the sample weight is stable at the end of the experiment, implying that all chemical reactions have been completed.

The onset temperatures (T_{on}) as shown in Fig. 14 can be used to indicate the resistance of the oil to thermal degradation determined by extrapolating the horizontal baseline at 1% degradation. The intercept of this line with the tangent to the downward portion of the weight curve was defined as the onset temperature. As the oil is oxidized, its onset temperature decreases [35].

Thermogravimetric data were used in characterizing the materials as well as in investigating the thermodynamics and kinetics of the reactions and transitions that resulting from the application of the oil samples. Currently, several methods are available in the literature that can be used to calculate the kinetic parameters. The kinetics used for the thermal conversion of the oil is similar to that reported by Torrente and Galán [51] and Jaber and Probert [52].

Two models may be used to evaluate the kinetic parameters of the oil samples. For the direct Arrhenius plot method for the non-isothermal kinetic parameters with constant heating rate ($B = dT/dt$), is given below:

$$\ln\left[\frac{1}{(1-x)}\frac{dx}{dt}\right] = \ln\frac{A}{B} - \frac{E_a}{RT}. \quad (1)$$

The plot $\ln[(1/(1-x))(dx/dt)]$ vs $1/T$ should give a straight line with slope $-E_a/R$, from which the activation energy, E_a, can be calculated.

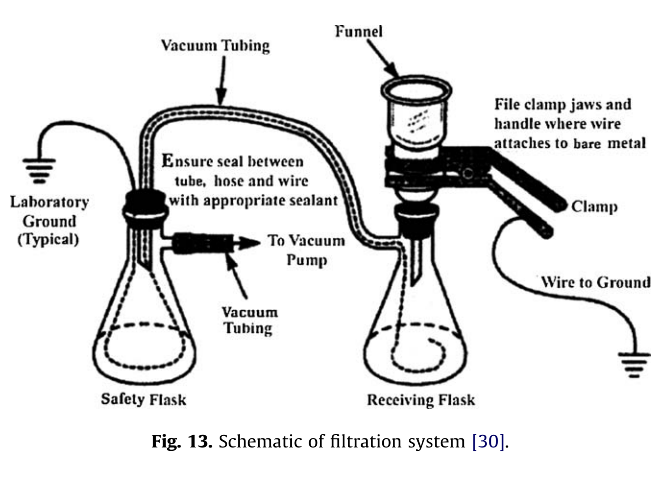


Fig. 13. Schematic of filtration system [30].

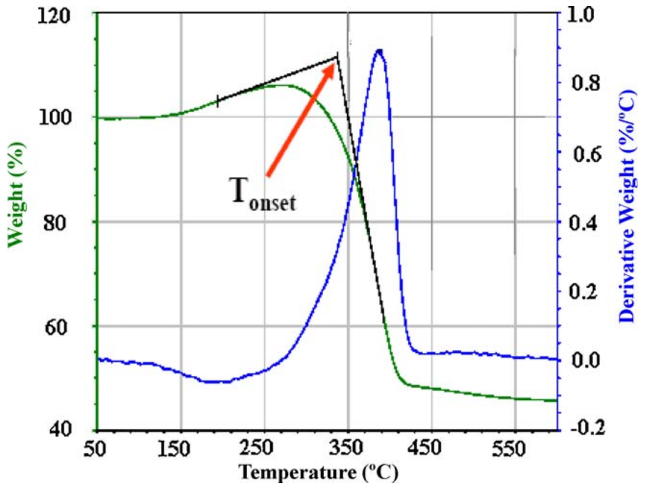


Fig. 14. TGA thermogram showing various parameters [35].

The integration method determines the overall reaction from the conversion vs temperature curves as discussed below:

$$\ln(-\ln(1-x)) = \ln\left[\frac{ART^2}{BE_a}\left(1-\frac{2RT}{E_a}\right)\right] - \frac{E_a}{RT}. \quad (2)$$

The plot $\ln[-\ln(1-x)]$ vs $1/T$ should give a straight line with slope $-E_a/R$, from which the E_a can be calculated. The amount of E_a gets decreases as the oil is oxidized.

The order of this reaction for the oil sample can be calculated as $n = (y - B - Cx)/z$ [18], where

$$y = \ln\left\{\left(-\frac{1}{w_0 - w_\infty}\right)\left(\frac{dw}{dt}\right)\right\}$$
$$x = \frac{1}{RT}$$
$$z = \ln\left(\frac{w - w_\infty}{w_0 - w_\infty}\right)$$
$$B = \ln A$$
$$C = -E_a.$$

Chand et al. [53] studied the effectiveness of TGA and found that TGA is an effective method, which is typically within ±1.5% relative to proton NMR method. Dantas et al. [54] studied the thermal stability and decomposition of biodiesel using TGA – DTA curves obtained using a simultaneous DTA/TG analyzer (SDT 2960, TA Instruments) in air and nitrogen (100 ml/min flow rate), in the temperature range 30–600 °C at a heating rate of 10 °C/min, using about 20 mg of sample in alumina crucibles.

The kinetic of corn biodiesel obtained from both the methanol and ethanol routes was conducted using dynamic heating to determine the mechanism, kinetic parameters and reaction order (n) and apparent activation energy (E_a). The thermogram indicated that corn oil was thermally stable up to 225 °C; the methanol biodiesel up to 139 °C and the ethanol biodiesel up to 159 °C in air. In nitrogen atmosphere, the corn oil was thermally stable up to 336 °C; the methanol biodiesel up to 145 °C and the ethanol biodiesel up to 169 °C. In both atmospheres, the ethanol biodiesel was more stable compared to other biodiesels as shown in Figs. 15–17.

The TG/DTG curves of corn oil in air in Fig. 15a show four mass loss steps which are assigned to the volatilization and/or combustion of the triglycerides. On the other hand, TG curve of

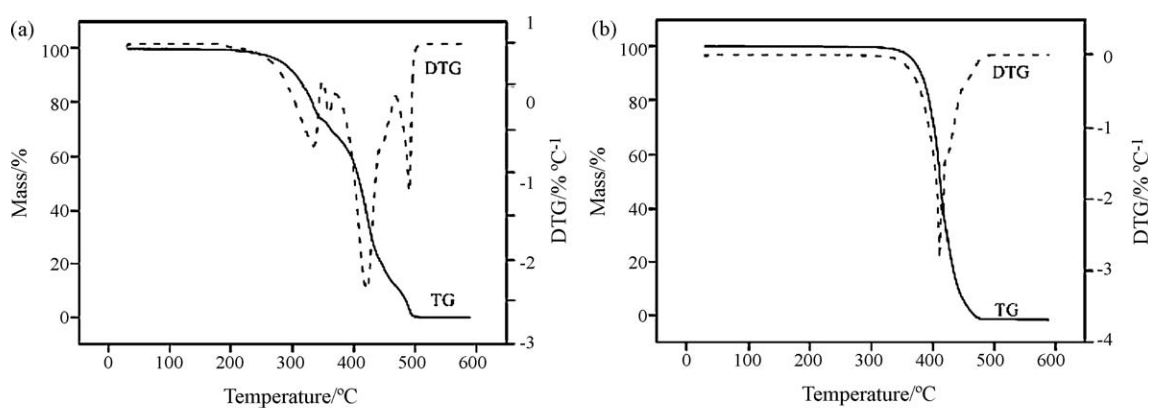


Fig. 15. TG/DTG curves of corn oil in (a) air and (b) N_2 atmosphere [54].

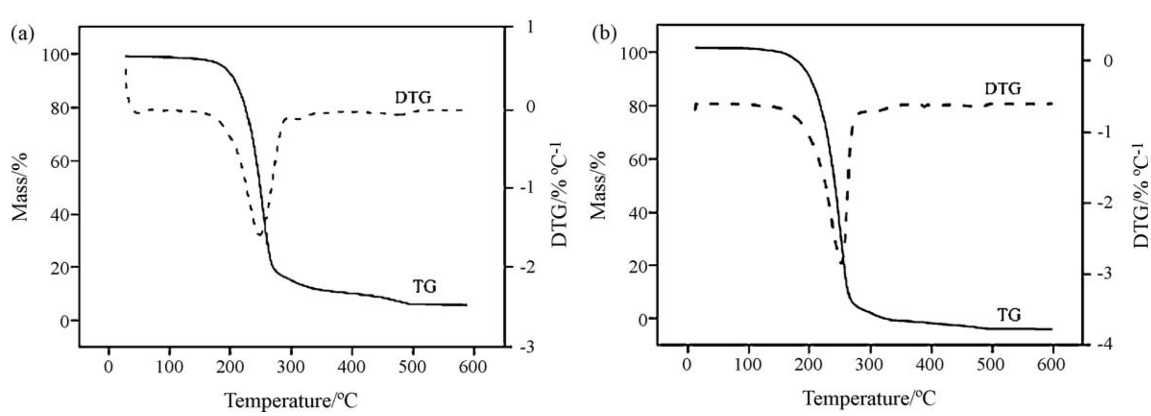


Fig. 16. TG/DTG curves of corn biodiesel obtained by the (a) methanol and (b) ethanol routes in air [54].

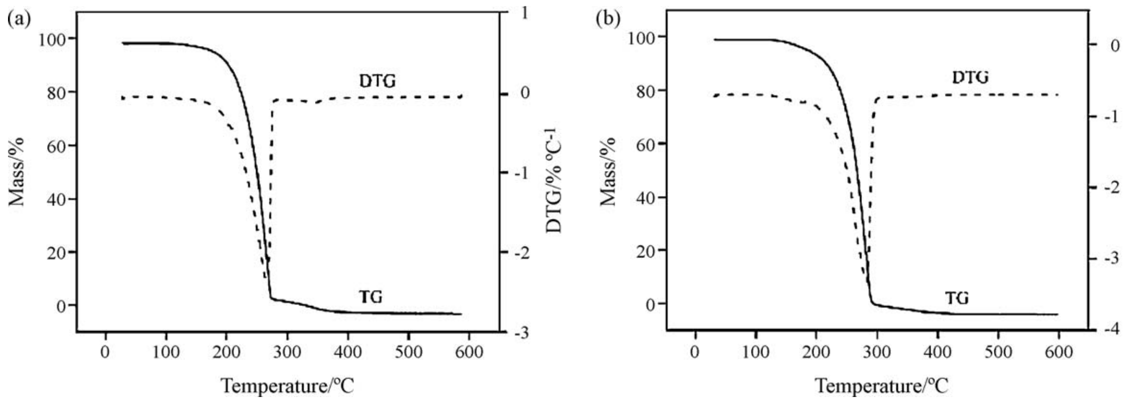


Fig. 17. TG/DTG curves of corn biodiesel obtained by the (a) methanol and (b) ethanol routes in nitrogen [54].

the corn oil in nitrogen (Fig. 15b) presents only one step attributed to the evaporization and/or pyrolysis of the triglycerides.

The TG/DTG curves of the biodiesel obtained using the methanol route in air (Fig. 16a) shows three steps which are attributed to the evaporization and/or combustion of the methyl esters, mainly, of the methyl linoleate, the most abundant component in the methanol biodiesel, in accordance with the high concentration of linoleic acid in corn oil. On the other hand, the TG/DTG curves of the biodiesel obtained from the ethanol route (Fig. 16b) in air displayed two thermal steps which are also ascribed to the evaporization and/or combustion of the ethyl esters, whose main component is ethyl linoleate as observed in the methanol route. The conversion of corn oil into methyl and ethyl esters was proved by the high concentrations of linoleates in the biodiesel samples. The gas chromatographic results indicated high amounts of methyl linoleate (66%) and ethyl linoleate (77%) in the methanol and ethanol biodiesel samples respectively.

The TG/DTG curves of the biodiesel produced by means of the methanol route (Fig. 17a) in nitrogen yielded two thermal steps ascribed to the evaporization and/or pyrolysis of the methyl esters, mainly, methyl linoleate while on the other hand, the TG/DTG curves of the ethanol biodiesel in nitrogen (Fig. 17b) show only one step related to the evaporization and/or pyrolysis of the esters, in this case the ethyl esters, mainly, ethyl linoleate.

From the various experiments as stated above Dantas et al. [54] found that corn oil was thermally stable up to 225 °C; the methanol biodiesel is stable up to 139 °C and the ethanol biodiesel is up to 159 °C in air. In nitrogen atmosphere the corn oil was thermally stable up to 336 °C; the methanol biodiesel up to 145 °C and the ethanol biodiesel up to 169 °C. In both atmospheres, the ethanol biodiesel was more stable.

Wan Nik et al. [35] studied the thermal stability of palm oil as energy transport media in a hydraulic system. The oils were aged by circulating the oil in an open loop hydraulic system at an isothermal condition of 55 °C for 600 h. In this study, two models were used to evaluate the kinetic parameters of the oil samples as direct Arrhenius plot method and integration method. Table 1 shows the details of various samples taken during experiment.

The thermal behavior and kinetic parameters of fresh and degraded palm oil, with and without oxidation inhibitor, were studied using the dynamic heating rate mode of a thermogravimetric analyzer. Viscosity, TAN and IV value were used to analyze the TGA data. The thermodynamic parameter of activation energy of the samples was determined using direct Arrhenius plot and integral methods. The result indicated that the activation energy values for the aged samples are always smaller than those of the fresh samples for both the methods. Further it is observed that the order of reaction decreases with heating time for all samples as shown in Fig. 18. It can be noted that the order of reaction increases slightly with the addition of an additive. The more the additive, the higher was the reaction order.

Table 1
Details of various palm oil (PO) samples taken during experiments [35].

S. no.	Sample Id	Additive and amount
1	A0	PO, no additive
2	B0	PO + 1.5% F10
3	C0	PO + 2% F10
4	D0	PO + 1.5% L135
5	E0	HO
6	A600	PO, no additive
7	B600	PO + 1.5% F10
8	C600	PO + 2% F10
9	D600	PO + 1.5% L135
10	E600	HO

The above figure shows the values of reaction order for all samples. '0' is showing that the sample is fresh and '600' is showing that sample is aged for 600 h. It was found that the order decreased with heating time for all samples. Interestingly, the order reduction for 'A' (palm oil without additive) is almost doubles that of the sample with additive. Not only the additive type but also the additive amount affects the order reduction. A higher amount of additive (oil C compared to oil B) reduces the order reduction.

Garcia et al. [55] studied the thermal stability of some vegetable oils obtained from Brazilian Cerrado native plants based on their high oleic acid contents using TGA. Three oils were selected for this study based on their high oleic acid content and potential for human consumption: amburana (*Amburana cearensis* (Fr. Allem) A.C. Smith) almond, baru (*Dypterix alata* Vog.) almond and pequi (*Caryocar brasiliense* Camb.) pulp oils. TG/DTG curves were obtained using Mettler Toledo TG/SDTA 851 e TG/SDTA equipment in synthetic air and nitrogen (100 ml/min) using alumina crucibles, at heating rate of 10 °C/min in the 25–650 °C temperature range

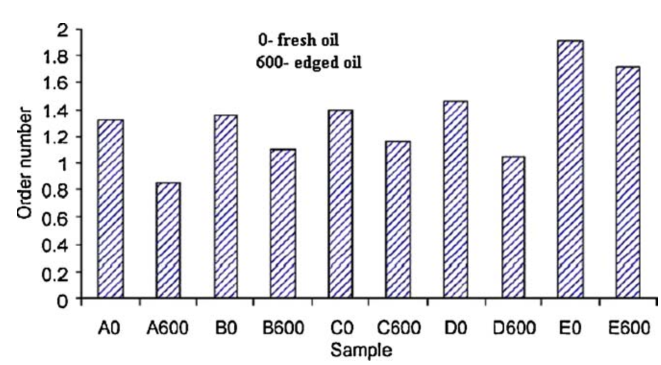


Fig. 18. Kinetic order for all samples [21].

with initial sample masses between 12 and 17 mg. It was found that the stabilities in nitrogen are similar. However pequi pulp oil has the highest stability followed by baru oil, while amburana oil is least stable. Thermal stability results can be related to the degree of unsaturation of the fatty acids constituting the oils. Normally, the higher the unsaturation in the oil, lower is the thermal stability. This could be explained by the lower boiling point of the unsaturated fatty acids compared to their saturated equivalents [56,57].

Freire et al. [58] evaluated the thermal behavior of the physic nut oil and biodiesel from several Brazilian crops using thermo-analytical techniques. Thermogravimetry (TG) and pressurized-differential scanning calorimetry (PDSC) were used to determine the applicability of physic nut biodiesel as fuel prepared by transesterification reaction with ethanol using oils from the seeds of different crops and homogeneous catalyst (KOH). The samples were designated as 2005/2006, 2006/2007, 2007/A and 2007/B on the basis of harvest period. As consequence, the 2005/2006 and 2006/2007 samples had the lower humidity among all the samples as they were stored for a longer time. The 2007/A and B samples differ from each other in terms of storage process. In the first case, the sample was exposed to solar radiation (summer crop), while another sample was stored under elevated environmental humidity (winter crop). TG/DTG and PDSC experiments were used to obtain information on the temperature-controlled combustion of the biofuels synthesized. TG/DTG curves were obtained using a simultaneous analyzer SDT 2960 (TA Instruments) under dry air atmosphere (100 ml/min) at a heating rate of 10 °C/min and temperature from 10 °C to 700 °C [59] using alumina pan. Physic nut oil and ethyl biodiesel from different crops were found thermally stable up to 203 °C (2007/B) and 108.9 °C (2007/A). The higher volatility of biodiesel, indicated by lower initial decomposition temperature, confirms the quality of physic nut biodiesel as biofuel. The oil and biodiesel from 2005/2006 crop were less stable than the others due to higher water content in the seeds. In general, the oxidation induction time (OIT) was 13 min for both oils and biodiesels except 2007/B sample with 33 min. These results suggested the physic nut biodiesel, as a prospective, renewable and biodegradable fuel for use in diesel engines. The results have shown that with increase in oxidation of biodiesel, the onset temperature decreases resulting in reduced fuel stability.

Dweck and Sampaio [60] studied the thermal decomposition of commercial vegetable oils in the presence of air by simultaneous TG/DTA and a plot of the estimated heats of combustion of olive, canola, sunflower and SOs as a function of their respective

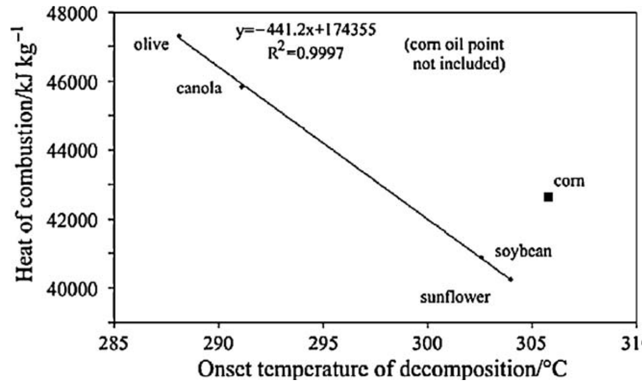


Fig. 19. Estimated heat of combustion of the oils as a function of the respective decomposition onset temperature [60].

extrapolated onset decomposition temperature indicated that higher is the onset temperature; the lower is the heat of combustion as evidenced by the fact that there is perfect linear correlation between stability and calorific value for all the above oils except corn oil, which does not follows this behavior. A plot of the estimated heats of combustion of olive, canola, sunflower and SOs as a function of their respective onset decomposition temperature is shown in Fig. 19.

It can be seen that, the higher is the onset temperature; the lower is the heat of combustion. As it can be noticed, the correlation coefficient is 0.9997 which indicates a perfect linear correlation between stability and calorific value for the studied oils except corn oil which does not follows this behavior. From the analysis of typical compositions of the studied oils, it is interesting to note that only olive oil is made up of saturated fatty acids molecules of 14 carbon atoms (1–3 mass%) with the highest content of those with C:16 atoms (7–16 mass%), which explains its lowest decomposition onset temperature. On the other hand, as corn oil consists of highest content of unsaturated fatty acid molecules with C:18 atoms, it shows the highest thermal stability among the oils. The lower is the molecular mass and number of double bonds in hydrocarbon chain, the higher is the carbon/hydrogen (C/H) mass ratio and the higher is its heat of combustion [21]. The mean IV of olive oil is significantly lower than the other analyzed oils [4]. This means that C/H mass ratio of olive oil is the highest among the studied oils and consequently, this fact explains its highest heat of combustion.

Table 2
Thermal stability experiments done by different researchers.

S. no.	Name of sample	Technique/methods used	Parameters adopted	Reference
1	Biodiesel	Rancimat test	Peroxide value, acid value and induction period	[16]
2	Methyl soyate	Viscosity meter and titration	Viscosity, acid value and peroxide value	[17]
3	Safflower, rapeseed and PO biodiesel	High-performance liquid chromatography (HPLC)	Tocopherols content	[18]
4	SO fatty acid methyl esters (SME) and used cooking oil fatty acid methyl esters (UCOME)	Rancimat test	OSI	[19]
5	SO and mixture of SO and palm oil	Rheometer and gas chromatograph	Viscosity and linoleic acid contents	[20]
6	Biodiesel	D 6468	Insolubles	[21]
7	Safflower oil	Rancimat test	Induction period	[28]
8	Biodiesel	D 5304-06	Insolubles	[31]
9	Biodiesel	D 5304-06	Insolubles	[32]
10	Biodiesel	D 5304-06	Insolubles	[33]
11	Biodiesel	D 5304-06	Insolubles	[34]
12	Palm oil	TGA/DTA	Kinetic order	[35]
13	Olive, canola, sunflower and soybean	TGA/DTA	Specific heat	[42]
14	Olive, canola, sunflower and soybean	TGA/DTA	Activation energy	[43]
15	Olive, canola, sunflower, soybean and PO	TGA/DTA	Temperature and enthalpy of crystallization	[44–47]
16	Olive, canola, sunflower and soybean	TGA/DTA	Oxidation induction time	[50]
17	Olive, canola, sunflower, soybean and PO	TGA/DTA	Onset temperature	[54–60]

The work carried out by various researchers on the thermal stability of various oils and biodiesels is, however, summarized in Table 2.

The above table summarizes the experiments of thermal stability carried out by various researchers. The thermal stability of biodiesel has been determined by using various methods which includes Rancimat test, gas chromatography, TGA/DTA, D 6468, D 5304-06, HPLC, etc. based on various thermal stability parameters such as PV, AV, viscosity, tocopherols contents, OSI, linoleic acid contents, insolubles, onset temperature, enthalpy of crystallization, oxidation induction time, etc. The most effective test parameters found for thermal stability are viscosity, linoleic acid contents, AV, onset temp and order of reaction but no perfect correlation has been found between these thermal stability parameters. Therefore, there is a need to develop co-relations between various thermal stability properties of vegetable oil and to study the effect of Rancimat induction period on various thermal stability parameters e.g. insoluble formation, viscosity, linoleic acid contents, onset temperature, order of reaction, etc. The results of such studies would prove to be valuable to establish correlations between the thermal stability of oils and their biodiesel and effect of various parameters on the thermal behavior.

5. Conclusion

The review of the work done so far has revealed that biodiesel is more prone to oxidation when exposed to higher temperature due to the formation of oxidation products like aldehydes, alcohols, shorter chain carboxylic acids, insolubles, gum and sediment in the biodiesel, which may often be responsible for fuel filter plugging, injector fouling, deposits formation in engine combustion chamber and various components of the fuel system. Most commonly used methods to investigate the thermal stability are Rancimat test, ASTM D 6408-08, D 5304-06 and TGA/DTA. Rancimat test has been suggested as an important method to measure the thermal stability of oils, fats and biodiesel fuels. Further the KF Coulometer has also been suggested as suitable method to measure the thermal as well as oxidation stability of vegetable oils. Large numbers of studies were devoted to the thermal stability of different oils using these methods. Further, TGA/DTA has been found as an effective method to check the deterioration of oil with respect to temperature using activation energy and order of reaction as the parameter to monitor the deterioration of oil. No co-relation have, however, been found in the literature between the results of various test methods. Much effort is required to be done in the field of biodiesel especially, increase in the thermal/oxidation stability of biodiesel from non-edible oils. Also the effect of blending of biodiesel with diesel on thermal stability needs to be checked. The effect of thermal parameters on storage and oxidation stability is, therefore, are important RandD areas to enhance and improve biodiesel stability for use in existing engines in future as a substitute of petroleum diesel.

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